

**A Structural Study of Some
Solid State
Silver Halide Phosphines**

Anders Cassel

Lund 1979

A STRUCTURAL STUDY OF SOME SOLID STATE SILVER HALIDE PHOSPHINES

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A Structural Study of Some Solid State Silver Halide Phosphines

Referat (sammandrag) Dimeric Chloro(bis(diphenylphosphinoethyl)sulphido)silver, dimeric Iodo(bis(diphenylphosphinoethyl)sulphido)silver, dimeric Chloro(1,5-bis(diphenylphosphine)pentane)silver, dimeric Chlorobis(triphenylphosphine)silver, Chlorotris(triphenylphosphine)silver have been investigated by X-ray diffraction methods.

According to stoichiometry silver(I) halide monotertiary phosphines give tetrameric, dimeric and monomeric molecular structures in the solid state. The silver:halide:phosphorus ratios are 1:1:1, 1:1:2 and 1:1:3, respectively. With ditertiary phosphines dimeric and monomeric structures are found. Silver prefers the coordination number four and the coordination polyhedron is a distorted tetrahedron. Steric effects seem to rule a change of the coordination number from four to three.

The silver-phosphorus bond distances increase with the number of coordinated phosphine ligands and are affected by the halide ion in the tetrameric molecules but not in the dimeric. The halide ions are three- or two-coordinated or terminal.

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INTRODUCTION

This review summarizes five papers (refs. 1-5) on X-ray structural studies of solid state silver halide monotertiary and ditertiary phosphine complexes:

The Crystal and Molecular Structures of Dimeric Chloro(bis(diphenylphosphino-ethyl)sulphido)silver, $(\text{AgClP}_2\text{SC}_{28}\text{H}_{28})_2$,¹

Dimeric Iodo(bis(diphenylphosphinoethyl)sulphido)silver,²

Dimeric Chloro(1,5-bis(diphenylphosphine)pentane)silver,³

Dimeric Chlorobis(triphenylphosphine)silver⁴ and

Chlorotris(triphenylphosphine)silver.⁵

The discussion of the structures will mainly deal with:

- the different molecular structure types of solid state silver halide tertiary phosphines according to stoichiometry and steric effects,
- variations in silver-phosphorus and silver-halide bond distances.

This study was started 1971 as a part of the project Structures of Complexes between Metal Halides and Phosphinothioethers or Related Ligands, initiated by late Professor Gerold Schwarzenbach, ETH, Zürich, Switzerland. Complexes of the phosphinothioether bis(diphenylphosphinoethyl)sulphide, $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_2$, abbreviated PSP, and 1,5-bis(diphenylphosphino)pentane, $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_5\text{P}(\text{C}_6\text{H}_5)_2$, abbreviated PC_5P , with some transition metals including mercury were investigated by X-ray diffraction methods, i.e. HgI_2PSP ,⁶ AgClPSP ,¹ AgIPSP ,² AgClPC_5P ,³ $\text{HgI}_2\text{PC}_5\text{P}$,⁷ and NiI_2PSP .⁸ In addition to these structures $\text{HgI}_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$ was also studied.⁹ Fäth (1976) has discussed PSP as a chelating ligand for different transition metal complexes.¹⁰ PSP is a potentially tridentate ligand and acts in this way in the compound NiI_2PSP . For HgI_2PSP and AgXPSP , $\text{X}=\text{Cl}$ and I , it acts as a bidentate ligand, the sulphur atom not being coordinated. The compound AgClPC_5P was

investigated to determine if a to AgXPSP similar dimeric molecular structure was formed. This was found although the dimer is more distorted.

To try to systematize the different structure types of silver halide tertiary phosphines with different compositions the compounds $\text{AgX}(\text{PPh}_3)_n$, $n=1, 2$ and 3 , $\text{Ph}=\text{C}_6\text{H}_5$, were synthesized. The compounds with $\text{X}=\text{Cl}$ were investigated by X-ray diffraction. During this work in 1975 Teo and Calabrese reported a cubane-like tetrameric structure of AgClPPh_3 .¹¹ They also reported that the corresponding iodine compound exists in two tetrameric modifications, a cubane-like and a chair-shaped (Fig. 1). In later papers they gave a more

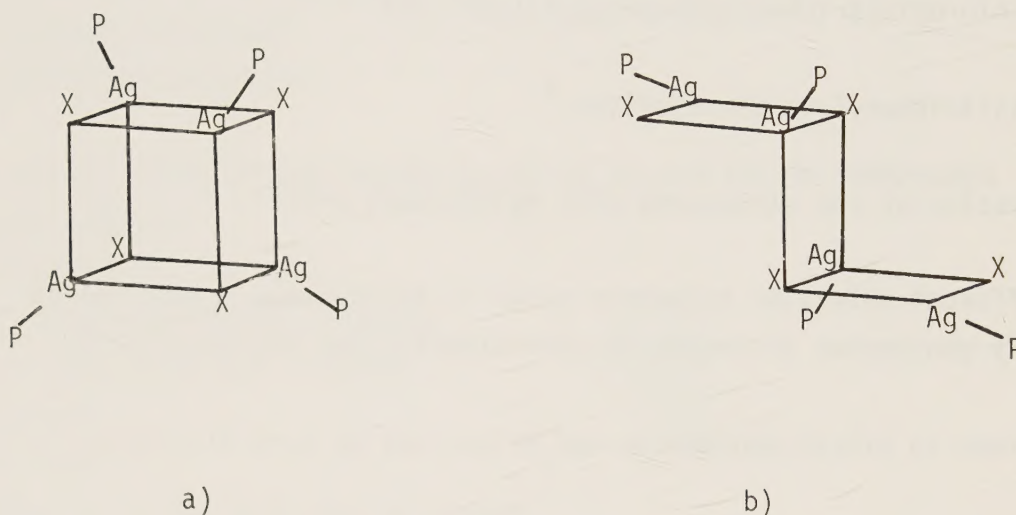


Fig. 1. Schematic drawings of a) the cubane-like AgClPPh_3 and AgIPPh_3
b) the chair-form of AgIPPh_3 .

detailed description of AgClPPh_3 ¹² and of differences between the two forms of AgIPPh_3 .¹³ During 1975-1976 Churchill et al. reported the tetrameric cubane-like structures of AgXPt_3 , $\text{X}=\text{Cl}$,¹⁴ Br ¹⁴ and I ,¹⁵ $\text{Et}=\text{C}_2\text{H}_5$. These structures were proposed 1937 by Mann, Wells and Purdie.¹⁶

Teo and Calabrese also reported the cubane-like structure of AgBrPPh_3 and in the same paper the structure of $\text{AgBr}(\text{PPh}_3)_2\text{CHCl}_3$.¹⁷ The latter compound is dimeric with two bridging bromine atoms.

EXPERIMENTAL

Preparation

Single crystals of AgXPSP, X=Cl and I, were kindly supplied by Professor Gerold Schwarzenbach. For preparation of the ligand and its metal complexes, see Degischer.¹⁸

The ligand PC₅P and AgClPC₅P were prepared by us following the method given by Degischer for PSP and AgXPSP.

The compounds AgCl(PPh₃)_n, n=1, 2 and 3, were prepared in our laboratory in the following way: Stoichiometric amounts of analytical grade reagents of silver nitrate, triphenylphosphine and tetraethylammonium chloride were mixed in a hot acetonitrile solution. Suitable single crystals were obtained on slow cooling of the solution. The compounds were analyzed for carbon and hydrogen content by conventional methods. There was good agreement between expected and experimental values.

Unit cell determination and intensity data collection

Two methods for determining the unit cell dimensions were employed. For AgXPSP and AgCl(PPh₃)₂ the powder method using Guinier-Hägg cameras of radii 40 mm ($\lambda(\text{CuK}\alpha)=1.54178 \text{ \AA}$) and 50 mm ($\lambda(\text{CuK}\alpha_1)=1.54051 \text{ \AA}$) were used. For AgClPC₅P and AgCl(PPh₃)₃ accurate θ angle values were determined on an Enraf-Nonius CAD4 four-circle diffractometer according to Danielsson, Grenthe and Oskarsson.¹⁹ Least-squares refinements revealed the cell dimensions. Table 1 gives crystal data of the investigated compounds.

Intensity data collections were performed on an Enraf-Nonius CAD4 computer-controlled four-circle diffractometer except for AgClPSP, for which the Weissenberg multiple film method was used. The computer-controlled data collecting was carried out using CuK α radiation and a graphite monochromator. Table 2 summarizes the data collection. The ω -2 θ scan technique was employed. The background was measured for one quarter of the scan time at each end of the peak-scan interval. During the collection standard reflections were regularly measured and the intensity variations with time were used to scale the intensities of the other reflections. A more detailed description of the equipment and the technique used is given by Svensson.²⁰

Table 1. Crystal data.

Formula and abbreviation	Symmetry and space group	Formula units per unit cell	Unit cell dimensions (Å, °)
(AgClP ₂ SC ₂₈ H ₂₈) ₂ AgClPSP	Triclinic p $\bar{1}$	1	a=11.560(4) α= 95.61(3) b=10.063(2) β=101.98(4) c=12.045(6) γ= 93.24(3)
(AgIP ₂ SC ₂₈ H ₂₈) ₂ AgIPSP	Triclinic p $\bar{1}$	1	a=11.796(2) α= 96.45(2) b=10.108(2) β=102.95(3) c=12.332(3) γ= 94.84(2)
(AgClP ₂ C ₂₉ H ₃₀) ₂ AgClPC ₅ P	Monoclinic P2 ₁ /n	4	a=13.428(1) b=33.263(4) β= 99.30(1) c=12.414(1)
(AgClP ₂ C ₃₆ H ₃₀) ₂ AgCl(PPh ₃) ₂	Triclinic p $\bar{1}$	1	a=10.308(5) α=113.36(4) b=12.608(4) β=110.29(3) c=13.893(6) γ= 75.02(3)
AgClP ₃ C ₅₄ H ₄₅ AgCl(PPh ₃) ₃	Monoclinic P2 ₁ /n	4	a=10.221(1) b=33.735(4) β= 89.78(1) c=13.374(3)

Table 2. Data collection and refinement.

Data collecting method	AgClPSP	AqIPSP	AgClPC ₅ P	AgCl(PPh ₃) ₂	AgCl(PPh ₃) ₃
Radiation	Weissenberg	CAD4	CAD4	CAD4	CAD4
	CuK α	CuK α	CuK α	CuK α	CuK α
$\lambda/\text{\AA}$	1.54178	1.54178	1.54178	1.54178	1.54178
μ/cm^{-1}	86	165	82	73	54
Number of reflections used in the refinement, m	2021	3659	4119	4821	7012
Number of parameters refined, n	158	159	305	181	263
$R=\Sigma F_o - F_c /\Sigma F_o $	0.064	0.048	0.071	0.065	0.054
$R_w=(\Sigma w(F_o - F_c)^2/\Sigma w F_o ^2)^{1/2}$	0.086	0.065	0.086	0.084	0.063
$S=(\Sigma w(F_o - F_c)^2/(m-n))^{1/2}$	0.3	1.3	1.8	2.9	1.9

Corrections were made for Lorentz, polarization and absorption effects. The data for AgIPSP and $\text{AgCl}(\text{PPh}_3)_3$ were also corrected for secondary extinction.

DETERMINATION AND REFINEMENT OF THE STRUCTURES

The three-dimensional Patterson function was used to locate the heavy atoms in all structures but AgIPSP. For this compound atomic parameters from the isostructural chlorine compound were used as starting parameters. Successive difference Fourier syntheses and least-squares refinements revealed the positions of all non-hydrogen atoms. The hydrogen atoms were not introduced in the refinements except for $\text{AgCl}(\text{PPh}_3)_3$, where they were geometrically positioned 1.00 Å from corresponding carbon atoms and with fixed positional and temperature parameters included in the final calculations. The quantity minimized in the least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, where w is the weight. Table 2 summarizes information on the refinements.

The atomic scattering factors were throughout taken for neutral atoms from Cromer and Waber²¹ for Ag in AgClPSP, from Hanson *et al.*²² for Cl, P, S and C in AgClPSP and for all atoms in AgIPSP and AgClPC_5P . For the atoms in $\text{AgCl}(\text{PPh}_3)_2$ and $\text{AgCl}(\text{PPh}_3)_3$ they were taken from International Tables for X-ray Crystallography, 1974.²³ All calculations were made on the UNIVAC 1108 computer in Lund. The programs used in the structure analyses are summarized by Elding²⁴ and Svensson.²⁰

DESCRIPTION OF THE STRUCTURES

The crystal structures

All compounds in this study consist of discrete dimeric or monomeric molecules in the solid state. The molecules are held together by van der Waals forces. Stereoscopic views of the packing of the molecules in the compounds AgXPSP, AgClPC_5P , $\text{AgCl}(\text{PPh}_3)_2$ and $\text{AgCl}(\text{PPh}_3)_3$ are shown in Figs. 2a, 3a, 4a and 5a.

The intermolecular distances have been calculated for $\text{AgCl}(\text{PPh}_3)_2$ and $\text{AgCl}(\text{PPh}_3)_3$ using geometrically positioned hydrogen atoms. For $\text{AgCl}(\text{PPh}_3)_2$ no hydrogen-hydrogen or hydrogen-chlorine distances shorter than 2.28 or 2.99 Å, respectively, are found. According to Pauling the van der Waals

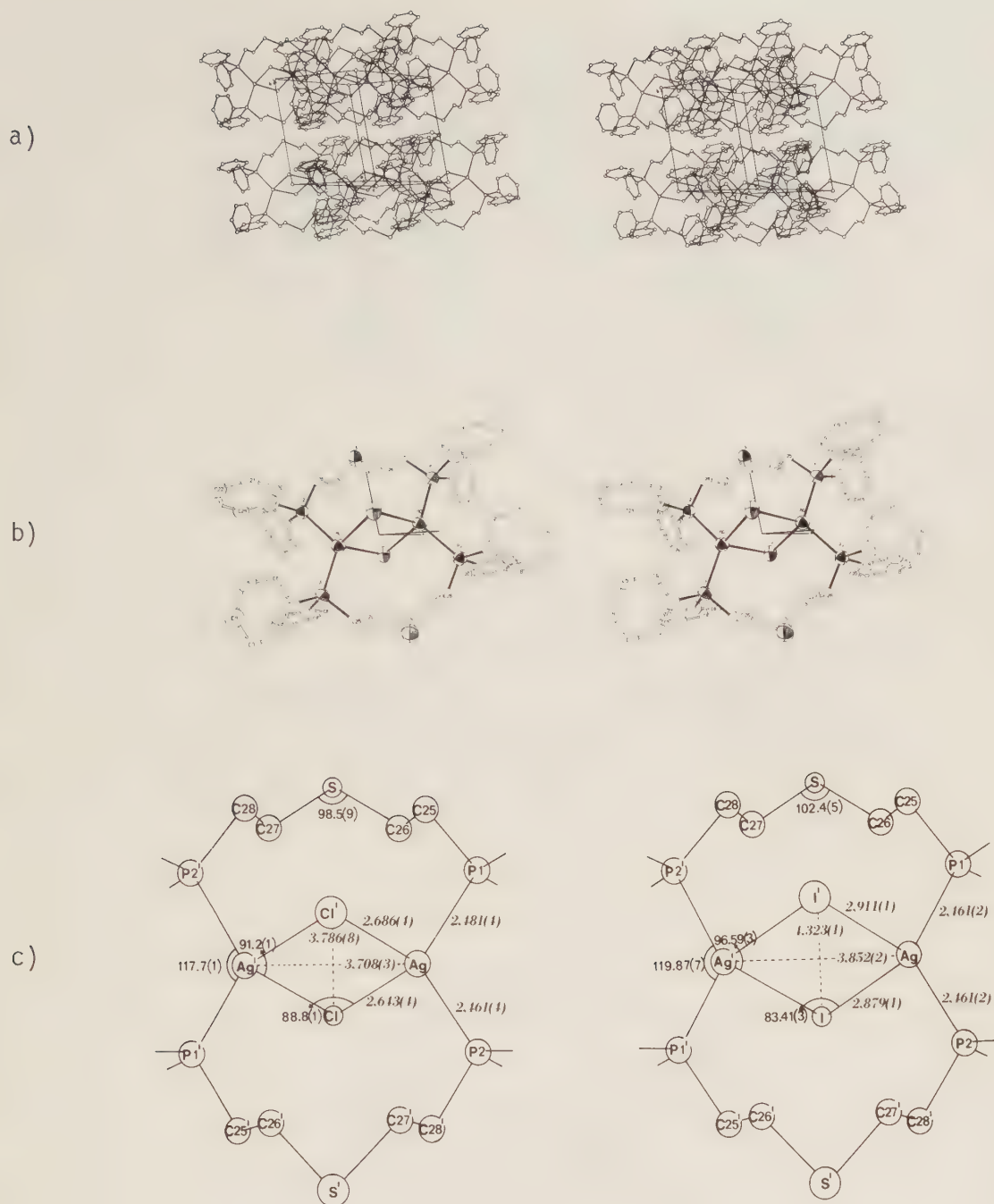


Fig. 2. Drawings of AgXPSP showing a) a stereoscopic view of the unit cell and the packing of the molecules, b) a stereoscopic view of the dimeric molecule and c) schematic drawings of fragments of the molecules of AgClPSP and AgIPSP. Selected distances (Å) and angles ($^{\circ}$) are denoted.

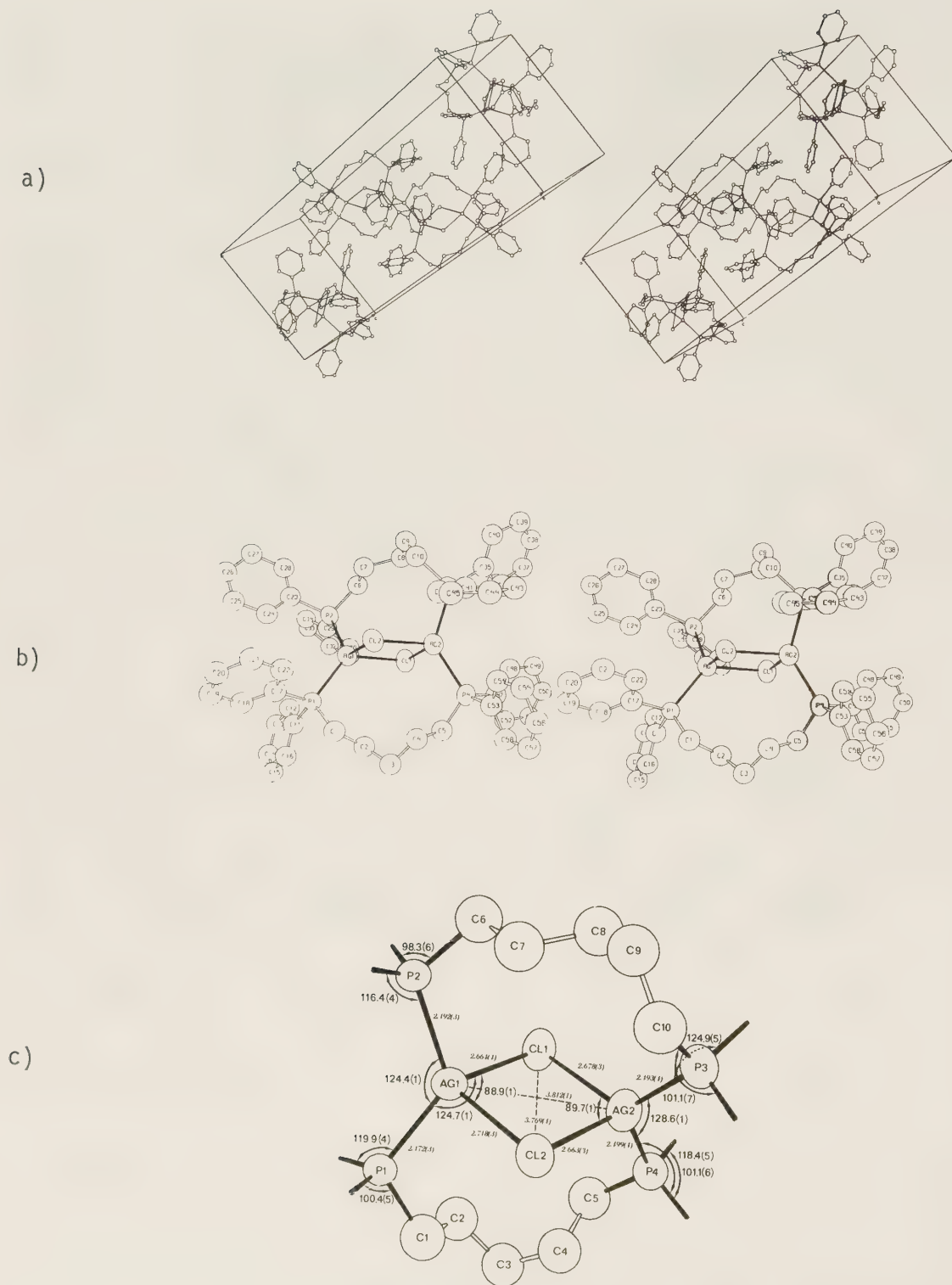


Fig. 3. Drawings of AgClPC_5P showing a) a stereoscopic view of the unit cell and the packing of the molecules, b) a stereoscopic view of the dimeric molecule and c) a schematic drawing of a fragment of the molecule. Selected distances ($\text{\AA}$) and angles ($^\circ$) are denoted.

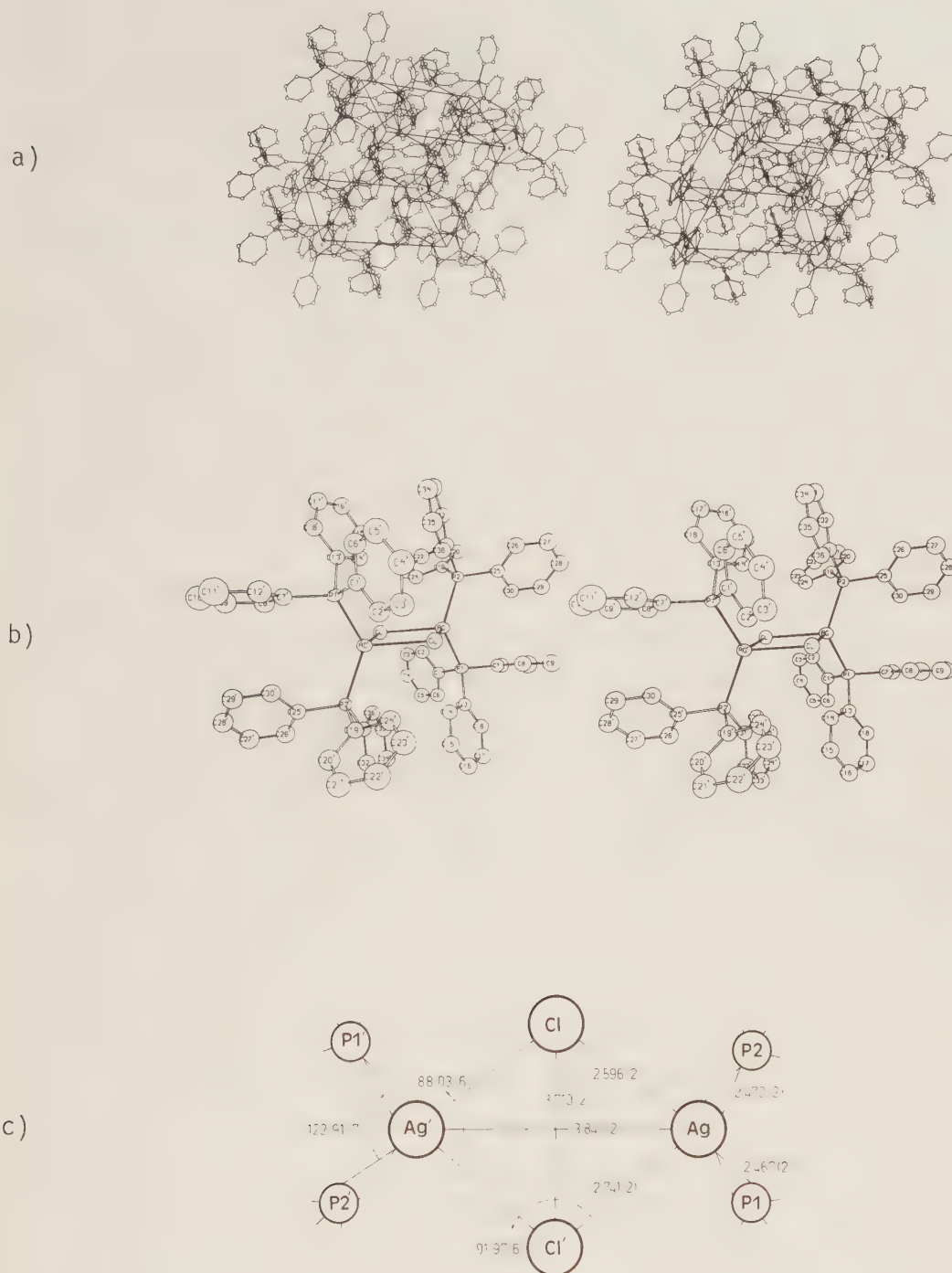


Fig. 4. Drawings of $\text{AgCl}(\text{PPh}_3)_2$ showing a) a stereoscopic view of the unit cell and the packing of the molecules. Origo of the drawn unit cell is positioned in $1/2, 0, 0$, b) a stereoscopic view of the dimeric molecule and c) a schematic drawing of a fragment of the molecule. Selected distances (Å) and angles ($^\circ$) are denoted.

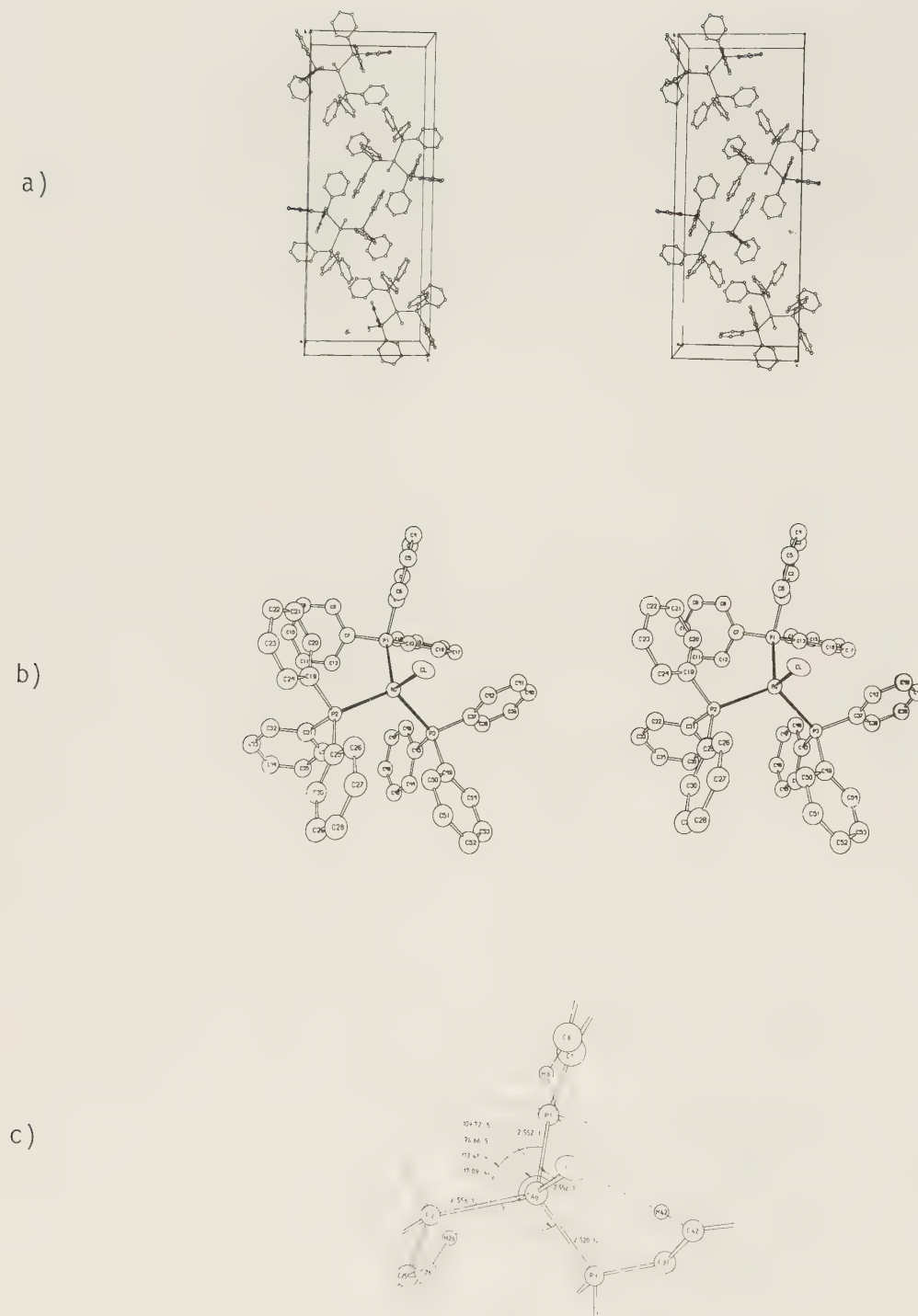


Fig. 5. Drawings of $\text{AgCl}(\text{PPh}_3)_3$ showing a) a stereoscopic view of the unit cell and the packing of the molecules, b) a stereoscopic view of the monomeric molecule and c) a schematic drawing of a fragment of the molecule. Selected distances (Å) and angles ($^\circ$) are denoted. The intramolecular H--Cl interactions are marked with broken lines.

distances are 2.4 and 3.0.²⁵ Baur suggests 1.00 Å for the van der Waals radius of hydrogen.²⁶ For $\text{AgCl}(\text{PPh}_3)_3$ no hydrogen-hydrogen or hydrogen-chlorine intermolecular distances shorter than 2.29 and 2.78 Å, respectively, are found.

The molecular structures

The molecular structures are described in refs. 1-5. Stereoscopic views of the molecules of AgXPSP , AgClPC_5P , $\text{AgCl}(\text{PPh}_3)_2$ and $\text{AgCl}(\text{PPh}_3)_3$ are shown in Figs. 2b, 3b, 4b and 5b, respectively. Selected distances and angles in the coordination polyhedra of silver are denoted in schematic drawings of parts of the molecules AgXPSP , AgClPC_5P , $\text{AgCl}(\text{PPh}_3)_2$ and $\text{AgCl}(\text{PPh}_3)_3$ in Figs. 2c, 3c, 4c and 5c.

The coordination polyhedron of silver is in all structures in this study a distorted tetrahedron. Besides the two halide atoms the ditertiary ligands PSP and PC_5P bridge the silver atoms in AgXPSP and AgClPC_5P . For $\text{AgCl}(\text{PPh}_3)_2$ the dimerization is fulfilled only with the two bridging chlorine atoms. The replacement of chlorine by iodine in AgXPSP gave small, but well detectable differences between the two structures. These differences are given in Fig. 2c and are discussed in ref. 2. In AgClPC_5P the $\text{P}_2\text{AgCl}_2\text{AgP}_2$ -core is much more distorted than in AgXPSP and $\text{AgCl}(\text{PPh}_3)_2$. In the latter compounds the four silver and halide atoms lie in a plane as a consequence of the symmetry. The same is of course true for the four phosphorus atoms (Figs. 2b and 4b). In AgClPC_5P the two silver and the two chlorine atoms lie approximately in a plane (ref. 3), but the planes through $\text{Ag}(1)$, $\text{P}(1)$, $\text{P}(2)$ and $\text{Ag}(2)$, $\text{P}(3)$, $\text{P}(4)$ (Fig. 3b) are not parallel like in the other dimeric structures, instead the angle between them is 42° . The first plane $\{\text{Ag}(1), \text{P}(1), \text{P}(2)\}$ has the angle 71° towards the best plane through $\text{Ag}(1)$, $\text{Ag}(2)$, $\text{Cl}(1)$ and $\text{Cl}(2)$ and the second $\{\text{Ag}(2), \text{P}(3), \text{P}(4)\}$, the angle 69° . This distortion, which manifests itself also in large P-Ag-P angles, is probably caused by the greater strain in the PC_5P ligand as compared to PSP. In $\text{AgCl}(\text{PPh}_3)_2$ (Fig. 4c) the angle $\text{P}(1)\text{-Ag-P}(2)$ is $122.91(7)^\circ$, which lies between the corresponding values of AgXPSP and AgClPC_5P .

While the silver-halide distances are fairly constant in AgXPSP and AgClPC_5P (Figs. 2c and 3c) they differ with almost 0.15 Å in $\text{AgCl}(\text{PPh}_3)_2$ (Fig. 4c).

The only monomeric structure in this study is that of $\text{AgCl}(\text{PPh}_3)_3$. Selected

distances and angles in the distorted tetrahedron of silver are shown in Fig. 5c. There are remarkable differences between $\text{AgCl}(\text{PPh}_3)_3$ and the corresponding copper compound, $\text{CuCl}(\text{PPh}_3)_3$.²⁷ In the latter the angles in the tetrahedral coordination of copper deviate slightly from the ideal tetrahedral value, 109.5° . Three independent molecules with a threefold axis along the Cu-Cl bond cause the angle range $108.41(7)$ - $110.51(6)^\circ$. For $\text{AgCl}(\text{PPh}_3)_3$, however, the angle range in one independent molecule is $96.66(5)$ - $117.09(4)^\circ$.

The coordination around phosphorus is in all structures in this study a distorted tetrahedron.¹⁻⁵ All C-P-C angles are smaller than 109.5° and all Ag-P-C angles, but one in AgClPC_5P , are greater than 109.5° . The structure of PPh_3 undergoes almost no changes with respect to P-C distances and C-P-C angles when acting as a complexing agent, compared to free PPh_3 in the solid state.²⁸ In Table 3 mean values of distances and angles in PPh_3 and in the triphenylphosphine ligands in AgClPPh_3 ,¹² $\text{AgCl}(\text{PPh}_3)_2$ and $\text{AgCl}(\text{PPh}_3)_3$ are given. The fact that the C-P-C angles in free PPh_3 are smaller than 109.5° is consistent with the great repulsion ability of lone-pair electrons compared to a pair in a single bond. However, when the lone-pair is engaged in a covalent bond these effects should be more or less cancelled and the C-P-C angles should be able to increase. Steric effects when a triphenylphosphine ligand enters the coordination sphere work in the opposite direction. The result is an almost levelling of the angle values.

Table 3. Mean values of P-C distances (Å) and C-P-C angles ($^\circ$) in free PPh_3 and in AgClPPh_3 , $\text{AgCl}(\text{PPh}_3)_2$ and $\text{AgCl}(\text{PPh}_3)_3$.

Compound	Mean P-C distance	Mean C-P-C angle
PPh_3	1.828(5)	103.0(7)
AgClPPh_3	1.817(15)	104.0(10)
$\text{AgCl}(\text{PPh}_3)_2$	1.824(6)	103.4(20)
$\text{AgCl}(\text{PPh}_3)_3$	1.826(2)	103.5(18)

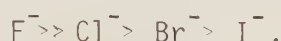
The angles in the phenyl rings deviate little from 120.0° and the mean carbon-carbon distances of each phenyl ring range between $1.38(4)$ - $1.41(4)$ Å.¹⁻⁵ The carbon atoms of the phenyl rings lie at most 0.04 Å outside the respective

best ring planes, except for one ring in AgClPC_5P , in which two atoms lie + 0.18 and -0.13 Å, respectively, from the plane.

BONDING AND COORDINATION AROUND SILVER IN SILVER HALIDE PHOSPHINES

General aspects

Metal ions can roughly be classified as hard, (a), or soft, (b), acceptors.^{29, 30} A class (a) or hard acceptor forms halide complexes with a metal to halide bond of mainly eletrostatic nature. The stability sequence is



Silver(I) forms in water complexes with the halide ions, but the stability of these complexes follow the sequence³¹



The silver to halide bond is in this case mainly covalent and therefore the stability sequence is reversed. Silver acts here as a class (b) or soft metal acceptor. According to these formulations the fluoride ion is classified as a hard and the iodine ion as a soft donor atom. In dimethylsulphoxide (DMSO) and acetonitrile (AN) the overall-formation constants (β_2) of dihalo complexes are almost levelled:³²

$$\begin{aligned} 11.9 &\leq \log \beta_2(\text{DMSO}) \leq 13.2 \\ 12.6 &\leq \log \beta_2(\text{AN}) \leq 15.2. \end{aligned}$$

This means that silver in these solvents is between the two classes.³³ For ligands containing donor atoms from the nitrogen group the stability of the soft metal complexes follow in water the sequence^{29,34}



For YPh_3 , $\text{Y}=\text{N}$, P , Sb and Bi , this sequence is for silver(I) fully confirmed also in DMSO solution.³⁵ For the reaction



the following overall-formation constants were obtained: $\log \beta_1 = 6.58(2)$, $\log \beta_2 = 10.73(3)$ and $\log \beta_3 = 13.17(2)$.

The great affinity of silver(I) to phosphorus is reflected in a large amount of synthesized silver(I) monotertiary and ditertiary phosphine compounds. Among these, halide compounds are also well represented.^{36,37,70} Few of these have been structurally investigated by three-dimensional X-ray analysis. For copper(I) several halide monotertiary and ditertiary phosphine structures have been determined, however.^{27,37,70,71}

In the copper phosphine complexes some authors propose little or no copper to phosphorus $d_{\pi} \rightarrow d_{\pi}$ back-bonding.²⁷ The copper ion usually accepts, if available, four electron-pairs from the donor atoms and forms σ -bonds in an approximately tetrahedral configuration. That $d_{\pi} \rightarrow d_{\pi}$ back-bonding is important is proposed by other authors.^{38,39} For silver(I) arsine complexes the higher stability of the first complex compared to the first amine complex is explained by the polarizing power of silver(I) and the higher polarizability of arsenic compared to nitrogen. No back-bonding from silver to arsenic is proposed.⁷² The role of $d_{\pi} \rightarrow d_{\pi}$ back-bonding from silver to phosphorus in silver halide phosphines is not clear.

In this study the bonding between silver and phosphorus will be considered to be of σ -character, but with the possibility of a weak $d_{\pi} \rightarrow d_{\pi}$ back-bonding element. The coordination around silver will be derived from linear sp , trigonal sp^2 and tetrahedral sp^3 hybrid orbitals of the metal atom.

The silver halide phosphines will from here on be discussed according to the stoichiometry of the complex and to the kind of tertiary phosphine present, *i.e.* monodentate or bidentate. The general formula AgXP_n , where n is an integer, X means a halide ion and P a phosphorus atom in a mono- or ditertiary phosphine, will be used in the systematization. Furthermore a halide ion with coordination number three, two or one will be called triply bridging, doubly bridging or terminal, respectively.

1

Chlorotris(triphenylphosphine)silver *

**
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Abstract. $\text{AgCl}(\text{P}_3\text{C}_{54}\text{H}_{45})$, monoclinic, $\text{P}2_1/\underline{n}$, $\underline{a}=10.221(1)$, $\underline{b}=33.735(4)$, $\underline{c}=13.374(3)$ Å, $\beta=89.78(1)^\circ$, $\underline{V}=4611$ Å³, $\underline{Z}=4$, $\underline{D}_\text{c}=1.34$, $\underline{D}_\text{o}=1.31$ Mg m⁻³. The crystal structure is built up by the packing of discrete monomeric molecules. In these Ag is tetrahedrally surrounded by three P atoms and one Cl atom. The coordination polyhedron is distorted, the angle range being $96.66(5)$ - $117.09(4)^\circ$. A comparison with the corresponding chlorotris(triphenylphosphine)copper(I) compound is made.

Introduction. Single crystals of $\text{AgCl}(\text{P}_3\text{C}_{54}\text{H}_{45})$, in the following denoted $\text{AgCl}(\text{PPh}_3)_3$, where $\text{Ph}=\text{C}_6\text{H}_5$, were obtained from stoichiometric amounts of AgNO_3 , $(\text{C}_2\text{H}_5)_4\text{NCl}$ and PPh_3 dissolved in warm CH_3CN and after slow cooling of the solution. One crystal of the approximate dimensions $0.30 \times 0.25 \times 0.20$ mm along $\underline{a}$, $\underline{b}$ and $\underline{c}$, was selected for the intensity measurements. The crystal could be described by the ten planes (010) , $(0\bar{1}0)$, (032) , $(0\bar{3}\bar{2})$, $(0\bar{3}2)$, $(03\bar{2})$, $(1\bar{3}0)$, $(\bar{1}30)$, (110) and $(\bar{1}\bar{1}0)$.

An Enraf-Nonius CAD4 computer-controlled four-circle diffractometer equipped with a graphite monochromator and $\text{CuK}\alpha$ radiation was used in the data collection. The ω - 2θ scan technique, with a scan interval $\Delta\omega=(0.60 + 0.25 \tan \theta)^\circ$, was employed. The background was measured for one quarter of the scan time at each end of the peak-scan interval. In the range $5 < \theta < 70^\circ$, 7012 reflections with $\underline{I} > 2\sigma(\underline{I})$, where $\sigma(\underline{I})$ is the standard deviation based on counting statistics, were measured. The data set was scaled

* Structures of Complexes Between Metal Halides and Phosphinothioethers or Related Ligands, IX.

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according to the intensities of two regularly measured standard reflections. The total intensity decrease was 10% and was linear with respect to exposure time. Corrections were also made for Lorentz, polarization, absorption [$\mu(\text{CuK}\alpha) = 5.4 \text{ mm}^{-1}$], anomalous dispersion and secondary extinction effects. Ag was located using the Patterson function. Successive electron density syntheses and least-squares refinements revealed the positions of Cl, P and C. Scattering factors for all atoms (neutral) were taken from International Tables for X-ray Crystallography (1974). The H atoms were geometrically positioned 1.00 Å from the corresponding C atoms, and with $B = 5.0 \text{ Å}^2$ included in the final refinements. The quantity minimized was $\sum w_i (|F_o| - |F_c|)^2$ giving final values of $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.054$ and $R_w = [\sum w_i (|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2} = 0.063$. Using $w_i^{-1} = \sigma^2(F_o) + 0.010 |F_o|^2 + 1.5$, the average values of $w_i (|F_o| - |F_c|)^2$ were made as constant as possible in different $\sin \theta$ and $|F_o|$ intervals. The value of $S = [\sum w_i (|F_o| - |F_c|)^2 / (m - n)]^{1/2}$ was 1.9. The secondary extinction parameter g was $0.69 \cdot 10^{-4}$. In the final difference synthesis no peak larger than 1.0 e Å^{-3} was found.

Final positional parameters are given in Table 1, selected interatomic distances in Table 2 and some intramolecular H--H, H--C and H--Cl distances in Table 3. All calculations were made on the UNIVAC 1108 computer in Lund.

Discussion. The crystal structure is built up by the packing of monomeric molecules of formula $\text{AgCl}(\text{PPh}_3)_3$. No H--H or H--Cl intermolecular distances shorter than 2.29 and 2.78 Å, respectively, are found. The van der Waals distances according to Pauling (1960) are 2.4 and 3.0 Å. According to Baur (1972) the radius of H is 1.00 Å giving the van der Waals distances 2.0 and 2.8 Å for H--H and H--Cl, respectively. These intermolecular distances thus have normal values.

A stereoscopic view of the molecule $\text{AgCl}(\text{PPh}_3)_3$ is shown in Fig. 1. Ag is tetrahedrally surrounded by one Cl atom and three P atoms from three PPh_3 ligands. As can be seen in Table 2 the tetrahedral angles around Ag deviate rather much from the ideal value, 109.5° . All angles P--Ag--Cl are close to or smaller than 109.5° , all P--Ag--P greater than 109.5° . In Fig. 2 some distances and angles in the distorted tetrahedron around Ag are shown.

* Lists of structure factors and vibrational parameters have been deposited with the British Library Lending Division as Supplementary Publication.

$\text{AgCl}(\text{PPh}_3)_3$ is as known to the author the only until now determined structure of a silver halide phosphine of stoichiometry 1:1:3. A discussion of the molecular structure according to similar Ag compounds is thus not possible. However, the analogous Cu compound, $\text{CuCl}(\text{PPh}_3)_3$, has been determined (Gill, et al., 1976). In this compound Cu is surrounded by three P atoms and one Cl forming an almost ideal tetrahedron. For three independent molecules in the unit cell the tetrahedral angle range $108.41(7)$ - $110.51(6)^\circ$ is found. There are indications that the differences between the two structures may be deduced from the difference between the tetrahedral covalent radius of Ag and Cu, viz. 0.17 Å (Pauling, 1960). The intramolecular repulsive H--H, H--C and H--Cl interactions between the ligands must be greater in the Cu compound; three equal, short intramolecular H--Cl distances in each independent $\text{CuCl}(\text{PPh}_3)_3$ molecule, 2.66, 2.74 and 2.74 Å, respectively, are reported. Corresponding distances in $\text{AgCl}(\text{PPh}_3)_3$ for one independent molecule are 2.70, 2.92 and 3.02 Å (Table 3). These distances are marked with broken lines in Fig. 2. If a plane is placed through H(6), H(26) and H(42) (Fig. 2), Ag is situated 2.00 Å from the plane, Cl 0.50 Å from it but on the opposite side. If Ag is replaced by Cu the Cu-Cl bond distance should decrease with about 0.17 Å and thereby cause more severe H--Cl interactions. Furthermore, the smaller Cu-P distances should enhance these repulsive interactions. Consequently, if only intramolecular interactions contribute to the differences between the structures the greater H--Cl repulsive interactions in $\text{CuCl}(\text{PPh}_3)_3$ seem to give smaller P-Cu-P and greater Cl-Cu-P angles as compared to the angles in $\text{AgCl}(\text{PPh}_3)_3$. However, intermolecular pseudo-graphitic stacking of some of the phenyl rings contribute to the stability of $\text{CuCl}(\text{PPh}_3)_3$ but the effect of this on the molecular geometry is difficult to propose. In $\text{AgCl}(\text{PPh}_3)_3$ no pseudo-graphitic stacking of phenyl rings is found. If greater halide ions would be introduced in the metal coordination spheres the repulsive H--X interactions should increase for both $\text{AgX}(\text{PPh}_3)_3$ and $\text{CuX}(\text{PPh}_3)_3$, X=Cl, Br and I. This should probably for the Ag compounds lead to a more regular tetrahedron around Ag, i.e. greater angles Cl-Ag-P and smaller P-Ag-P, but for the copper compounds to a more distorted polyhedron, i.e. greater Cl-Cu-P angles and smaller P-Cu-P angles. For sufficiently bulky PR_3 ligands, R=substituent on P, the formation of a $\text{AgX}(\text{PR}_3)_3$ complex in the solid state should probably fail for steric reasons.

The Ag-P bond distances increase as the number of P atoms around Ag increases.

In AgClPPh_3 (Teo and Calabrese, 1976) the Ag-P distances are 2.376(3) and 2.388(3) Å, in $\text{AgCl(PPh}_3)_2$ (Cassel, 1979) 2.467(2) and 2.472(2) Å and in $\text{AgCl(PPh}_3)_3$ 2.520(1), 2.556(1) and 2.552(1) Å, (Table 2, Fig. 2). This is expected as the acceptor ability of Ag decreases with an increasing number of coordinated good donor atoms.

The Ag-Cl bond distance, 2.552(1) Å, in $\text{AgCl(PPh}_3)_3$ is slightly longer than the expected one, 2.51 Å (Pauling, 1960).

Distances and angles in the coordination of P have expected values. All Ag-P-C angles are greater than 109.5° and all C-P-C angles are smaller than 109.5° (Table 2). The mean P-C distance is 1.825(2) Å.

The C-C-C angles in the phenyl rings deviate little from 120.0° and the mean C-C distances vary between 1.373(13)-1.394(3) Å (Table 2).

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Table 1. Fractional coordinates ($\times 10^4$, for Ag, Cl, P(1), P(2) and P(3) $\times 10^5$)
in AgCl(P₃C₅₄H₄₅)
 Standard deviations are given in parentheses.

	<u>x</u>	<u>y</u>	<u>z</u>		<u>x</u>	<u>y</u>	<u>z</u>
Ag	20069(4)	38906(1)	27128(3)	C(26)	1572(6)	4567(2)	5279(4)
Cl	-2422(13)	41903(4)	30576(12)	C(27)	1508(6)	4927(2)	5765(5)
P(1)	17463(13)	31945(4)	19929(10)	C(28)	2628(6)	5099(2)	6149(4)
P(2)	28025(12)	38956(4)	45221(9)	C(29)	3821(6)	4910(2)	6052(5)
P(3)	30271(13)	43858(4)	15346(10)	C(30)	3895(6)	4542(2)	5577(4)
C(1)	85(5)	3002(2)	1926(4)	C(31)	4468(5)	3723(1)	4736(4)
C(2)	-249(6)	2687(2)	1311(4)	C(32)	4845(6)	3496(2)	5550(5)
C(3)	-1519(7)	2544(2)	1284(5)	C(33)	6170(8)	3402(2)	5674(5)
C(4)	-2473(7)	2722(2)	1862(5)	C(34)	7091(8)	3543(2)	5015(5)
C(5)	-2147(8)	3031(2)	2475(6)	C(35)	6735(7)	3765(2)	4221(5)
C(6)	-877(6)	3174(2)	2509(5)	C(36)	5424(6)	3851(2)	4056(4)
C(7)	2632(5)	2807(2)	2655(4)	C(37)	2251(5)	4437(2)	311(4)
C(8)	2094(6)	2447(2)	2930(4)	C(38)	2944(6)	4455(2)	-585(4)
C(9)	2821(7)	2173(2)	3499(5)	C(39)	2250(7)	4508(2)	-1488(5)
C(10)	4082(8)	2270(2)	3760(5)	C(40)	930(8)	4536(2)	-1469(6)
C(11)	4624(7)	2621(2)	3503(5)	C(41)	228(8)	4512(2)	-598(6)
C(12)	3912(6)	2892(2)	2954(5)	C(42)	897(6)	4463(2)	307(5)
C(13)	2287(6)	3143(2)	695(4)	C(43)	4734(5)	4264(2)	1266(4)
C(14)	3050(9)	2846(3)	342(6)	C(44)	5778(6)	4509(2)	1484(4)
C(15)	3404(11)	2837(3)	-692(8)	C(45)	7058(7)	4373(2)	1368(5)
C(16)	2982(10)	3133(3)	-1300(7)	C(46)	7286(8)	4002(2)	1036(6)
C(17)	2208(8)	3419(2)	-971(6)	C(47)	6264(8)	3755(2)	783(6)
C(18)	1837(6)	3425(2)	36(5)	C(48)	4981(7)	3887(2)	907(5)
C(19)	1760(5)	3582(1)	5304(4)	C(49)	3032(5)	4900(2)	1961(4)
C(20)	1377(6)	3225(2)	4915(4)	C(50)	2551(6)	4984(2)	2902(5)
C(21)	525(7)	2977(2)	5425(5)	C(51)	2521(8)	5373(2)	3265(5)
C(22)	20(6)	3090(2)	6334(5)	C(52)	2953(8)	5680(2)	2658(6)
C(23)	384(7)	3441(2)	6727(5)	C(53)	3402(7)	5599(2)	1689(5)
C(24)	1256(7)	3692(2)	6233(5)	C(54)	3449(6)	5211(2)	1342(5)
C(25)	2777(5)	4369(1)	5185(3)				

Table 2. Interatomic distances (Å) and angles (°) in AgCl(P₃C₅₄H₄₅)

Standard deviations are given in parentheses. For notation, see Fig. 1.

Silver coordination

Ag-Cl	2.552(1)
-P(1)	2.552(1)
-P(2)	2.556(1)
-P(3)	2.520(1)

Phosphorus coordination

P(1)-Ag	2.552(1)
-C(1)	1.822(5)
-C(7)	1.823(5)
-C(13)	1.827(6)

Phosphorus coordination

P(2)-Ag	2.556(1)
-C(19)	1.826(5)
-C(25)	1.826(5)
-C(31)	1.823(5)

P(3)-Ag	2.520(1)
-C(37)	1.829(5)
-C(43)	1.826(6)
-C(49)	1.825(5)

Mean C-C distances in the phenyl rings*

1.381(3)	1.384(7)	1.373(13)	1.377(7)	1.390(4)	1.386(7)
1.388(9)	1.380(7)	1.394(3)			

Mean C-C-C angles in the phenyl rings*

119.9(3)	119.9(5)	120.0(5)	119.8(6)	120.0(2)	119.9(3)
120.0(4)	120.0(3)	120.0(2)			

Angles in the distorted tetrahedra around the Ag and P atoms

Cl-Ag-P(1)	109.72(5)	Ag-P(1)-C(1)	116.5(2)
Cl-Ag-P(2)	96.66(5)	Ag-P(1)-C(7)	115.1(2)
Cl-Ag-P(3)	102.75(5)	Ag-P(1)-C(13)	114.5(2)
P(1)-Ag-P(2)	113.41(4)	C(1)-P(1)-C(7)	103.5(2)
P(1)-Ag-P(3)	114.69(5)	C(1)-P(1)-C(13)	101.4(3)
P(2)-Ag-P(3)	117.09(4)	C(7)-P(1)-C(13)	104.1(3)

Ag-P(2)-C(19)	110.6(2)	Ag-P(3)-C(37)	116.2(2)
Ag-P(2)-C(25)	117.5(2)	Ag-P(3)-C(43)	111.5(2)
Ag-P(2)-C(31)	116.6(2)	Ag-P(3)-C(49)	115.8(2)
C(19)-P(2)-C(25)	102.7(2)	C(37)-P(3)-C(43)	105.2(2)
C(19)-P(2)-C(31)	105.6(2)	C(37)-P(3)-C(49)	101.1(2)
C(25)-P(2)-C(31)	102.4(2)	C(43)-P(3)-C(49)	105.8(2)

* cf. (Cassel, 1979)

Table 3. Selected intramolecular distances (Å) between atoms of different ligands in AgCl(P₃C₅₄H₄₅)

H--H distances <3.00 Å

H(C50)-H(C26)	2.87	H(C42)-H(C18)	2.99
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H--C distances <3.00 Å

H(C20)-C(7)	2.58	H(C50)-C(25)	2.86
H(C20)-C(8)	2.95	H(C50)-C(26)	2.75
H(C20)-C(12)	2.95	H(C18)-C(37)	2.90
H(C48)-C(13)	2.76	H(C18)-C(42)	2.81
H(C48)-C(18)	2.80	H(C17)-C(39)	2.99

H--Cl distances <3.40 Å

H(C6)-Cl	2.70	H(C42)-Cl	3.02
H(C26)-Cl	2.92	H(C50)-Cl	3.20

Figure captions

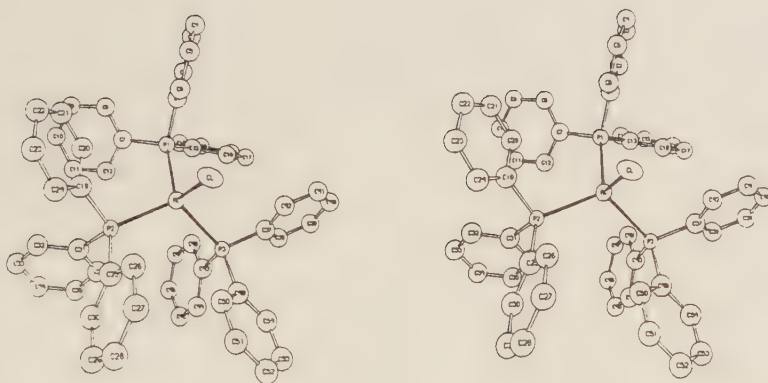


Fig. 1. A stereoscopic view of the molecule $\text{AgCl}(\text{P}_3\text{C}_{54}\text{H}_{45})$.

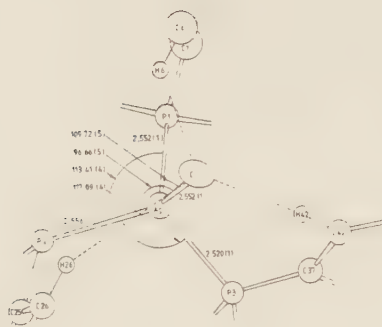


Fig. 2. A schematic drawing of a fragment of the molecule $\text{AgCl}(\text{P}_3\text{C}_{54}\text{H}_{45})$. Selected distances (Å) and angles ($^\circ$) are denoted. The intramolecular H...Cl repulsive interactions are marked with broken lines:

Vibrational parameters for the Ag, Cl, P and C atoms. The expression for the anisotropic thermal parameters of Ag, Cl and P is of the form: $\exp(-(\underline{h}^2 \beta_{11} + \underline{k}^2 \beta_{22} + \underline{l}^2 \beta_{33} + 2\underline{hk} \beta_{12} + 2\underline{hl} \beta_{13} + 2\underline{kl} \beta_{23}))$. The β_{ij} values for Ag, Cl, P(1), P(2) and P(3) are multiplied by 10^5 . Isotropic thermal parameters, $\underline{B}$ ($\text{\AA}^2$), are given for C. Estimated standard deviations are given in parentheses.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ag	629(4)	69(1)	392(2)	5(1)	47(2)	10(1)
Cl	574(12)	99(2)	858(11)	39(3)	8(9)	-87(3)
P(1)	722(13)	64(1)	425(7)	14(3)	23(8)	-21(2)
P(2)	622(12)	63(1)	327(6)	1(3)	-1(7)	6(2)
P(3)	609(12)	71(1)	388(7)	-29(3)	5(8)	28(2)

	B		B		B		B
C(1)	3.1(1)	C(7)	3.2(1)	C(13)	3.5(1)	C(19)	2.9(1)
C(2)	4.1(1)	C(8)	4.1(1)	C(14)	6.6(2)	C(20)	3.9(1)
C(3)	4.6(1)	C(9)	5.3(1)	C(15)	9.0(3)	C(21)	4.8(1)
C(4)	5.5(1)	C(10)	5.6(1)	C(16)	7.4(2)	C(22)	4.3(1)
C(5)	5.6(2)	C(11)	5.2(1)	C(17)	6.0(2)	C(23)	5.1(1)
C(6)	4.4(1)	C(12)	4.3(1)	C(18)	4.4(1)	C(24)	4.6(1)
C(25)	2.7(1)	C(31)	2.9(1)	C(37)	3.2(1)	C(43)	3.2(1)
C(26)	3.7(1)	C(32)	4.2(1)	C(38)	4.1(1)	C(44)	4.0(1)
C(27)	4.2(1)	C(33)	5.5(1)	C(39)	5.3(1)	C(45)	5.1(1)
C(28)	4.0(1)	C(34)	5.5(1)	C(40)	5.8(2)	C(46)	5.5(1)
C(29)	4.2(1)	C(35)	4.9(1)	C(41)	5.7(2)	C(47)	5.9(2)
C(30)	3.5(1)	C(36)	3.9(1)	C(42)	4.3(1)	C(48)	5.0(1)
C(49)	3.1(1)	C(50)	4.4(1)	C(51)	5.6(2)	C(52)	5.8(2)
C(53)	5.4(1)	C(54)	4.3(1)				

Structure factor table. Observed and calculated structure factors. The columns are $\underline{h}$, $10 \times |\underline{F}_o|$ and $10 \times |\underline{F}_c|$.

AgXP-type

Churchill and co-workers and Teo and Calabrese have investigated solid state structures of this type for both silver(I) and copper(I) compounds (for refs., see Table 4). The structures consist of tetrameric $M_4X_4(PR_3)_4$ molecules, R= Et or Ph. In the tetrameric arrangement the Ag_4X_4 and Cu_4X_4 cages are either of a cubane form, a distorted cubane form, or of a chair form (Fig. 1). In Table 4 twelve investigated compounds are systematized according to formula and form. In Table 5 Ag-P, Ag-X and X-X distances in the seven silver struc-

Table 4. A systematization of the tetrameric compounds of MXP-type, M=Cu and Ag, X=Cl, Br and I, according to formula and form.

Compound	$AgClPEt_3$	$CuClPEt_3$	$AgClPPh_3$	$CuClPPh_3$
Form	cubane	cubane	cubane	cubane
Reference	14	40	12	42
Compound	$AgBrPEt_3$	$CuBrPEt_3$	$AgBrPPh_3$	$CuBrPPh_3(CHCl_3)_2$
Form	cubane	cubane	cubane	chair
Reference	14	40	17	43
Compound	$AgIPEt_3$	$CuIPEt_3$	$AgIPPh_3$	$CuIPPh_3$
Form	cubane	cubane	cubane/chair	chair
Reference	15	41	13	44

tures are given. From Tables 4 and 5 it can be concluded that:

- introducing bulky phosphines and heavy halide ions increases the stability of the chair form,¹³
- the intramolecular halogen to halogen distances are close to or greater than the sum of the van der Waals radii: Cl--Cl=3.60, Br--Br=3.90 and I--I=4.30 Å,²⁵
- the silver to phosphorus distances increase in the serie Cl < Br < I,

Table 5. Distances (Å) in silver halide phosphines of AgXP-type. For Ag-X and X-X the maximum and minimum values are given, if available. For references, see Table 4.

Compound	Ag-P	Ag-X	Ag-X (mean value)	X-X
AgClPEt ₃ ^a	2.390(2)	2.821(2) 2.300(2)	2.65(30)	3.926(3)
AgClPPh ₃	2.376(3) 2.388(3)	2.760(3) 2.532(3)	2.65(9)	4.031(3) 3.649(5)
AgBrPEt ₃ ^a	2.402(5)	2.897(5) 2.422(7)	2.73(27)	4.201(3)
AgBrPPh ₃	2.415(5) 2.429(2)	2.962(1) 2.677(1)	2.80(12)	4.200(1) 3.964(2)
AgIPet ₃	2.438(2) 2.459(4)	2.919(1) 2.918(1)	2.919(1)	4.768(1) 4.723(1)
AgIPPh ₃ (cubane)	2.462(5) 2.456(5) 2.456(5)	3.034(2) 2.836(2)	2.91(12)	4.801(2) 4.399(2)
AgIPPh ₃ (chair)	2.430(3) ^b 2.454(3)	2.995(1) 2.835(1)	2.92(11)	4.763(1) 4.505(1)

a) Ag has a threefold disordered position around the threefold axis, P and X have not.

b) Ag is three-coordinated.

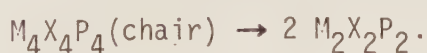
- the silver to halide distances are close to or greater than the sum of the tetrahedral covalent radius of silver, 1.52 Å, and the covalent single bond radius of gaseous chlorine, 0.99, bromine, 1.14, and iodine, 1.33 Å.²⁵

The last two conclusions will be discussed in the sections Variations in the Ag-P bond distances, p.26, and Variations in the Ag-X bond distances, p.28, respectively, of this study.

Teo and Calabrese suggest that the increasing intramolecular repulsive interactions between for example X--X and R--X, X=halide ion and R=substituent on P, when bulkier phosphines and heavier halide ions are introduced are responsible for the stereochemical variation:¹³



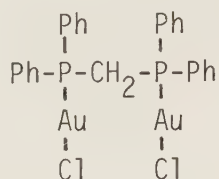
Recently Churchill and Rotella have shown that with the very bulky ligand tricyclohexylphosphine the formation of the tetrameric $Cu_4Cl_4(P(Cy)_3)_4$ structure in the solid state failed.⁴⁵ Instead a dimer with doubly bridging chlorine ions and three-coordinated copper was formed. They suggest that the above proposed stereochemical variation can be extended with a dissociation step in which the chair form is thought to be divided into two dimeric molecules:



Support for this tetrameric-dimeric variation in the solid state can be found in reports concerning silver halide tertiary phosphines in solution. From measurements in benzene solutions the following molecular species are proposed: $Ag_4X_4(PMe_3)_4$, X=Cl,⁴⁶ I,⁴⁷; $Ag_4I_4(PR_3)_4$, R=Et, n-Pr and n-Bu¹⁶ and $Ag_4I_4(PEt_2Ph)_4$ (refs. 48 and 57). In CH_2Cl_2 $AgCl(PhP(\overset{CH_2}{\underset{CH_2}{>}}C_6H_4))$ is dimeric.⁴⁹ $AgXP(t-Bu)_3$ is monomeric for X=Cl but dimeric for X=Br² in chloroform and 1,2-dichlorethane.⁵⁰ Schmidbaur and Aly have recently reported that $AgXP(t-Bu)_3$ probably is tetrameric for X=Cl in benzene and dimeric for X=Br in benzene and chloroform.⁷⁴

It could be of interest to determine the structures of $AgXPR_3$, where R=cyclohexyl, t-butyl or other bulky substituents, to try to confirm the formation of dimeric three-coordinated silver halide phosphine complexes in the solid state.

For gold(I) halide monotertiary phosphines of AuXP stoichiometry no tetrameric or dimeric structures have been found in the solid state. AuClPPh₃ is monomeric and the coordination around Au is approximately linear.⁵¹ Also in the compound Au₂Cl₂(Ph₂PCH₂PPh₂) the coordination is linear in the following way:⁵²



AgXP₂-type, monodentate ligands

There are only two structure determinations of solid state compounds of stoichiometry AgXP₂ viz. AgCl(PPh₃)₂⁴ and AgBr(PPh₃)₂CHCl₃.¹⁷ For both of them dimeric molecular structures are found (Fig. 4b). Analogues copper and gold complexes are monomeric viz. CuBr(PPh₃)₂(C₆H₆)_{1/2}⁵³ and AuCl(PPh₃)₂(C₆H₆)_{1/2}⁵⁴ and dimeric viz. CuI(P(C≡C-C₆H₅))₂ (ref. 73). A dimeric copper(I) arsine complex with four-coordination around copper has been found for the compound CuCl(AsMe₂Ph)₂.²⁷ There are copper halide phosphine structures reported to be dimeric, but with the stoichiometry Cu₂X₂P₃.^{27,38} In these structures copper is both three- and four-coordinated.

According to these results the following molecules seem to be appropriate in a systematization of solid state structures of silver and copper halide tertiary phosphines:



In the thought dimeric dissociation or monomeric association reactions two M-X bonds are broken or formed. In the thought phosphine elimination or addition reactions an M-P bond is broken or formed.

For copper, MXP₂, P₂MX₂MP₂ and P₂MX₂MP molecules are formed in the solid state as mentioned above.

For the two silver compounds the molecule P₂MX₂MP₂ is formed. In both structures intramolecular hydrogen-halogen interactions are reported.^{4,17} For the chlorine compound the differences in the Ag-Cl bond distances (Fig. 4c and Table 6) indicate a dissociation to or an association from two monomeric molecules. In the bromine compound, however, the Ag-Br bond distances are equal.

The differences in Ag-P distances, 2.513(7) and 2.479(6) Å, indicate that the Ag-P bonds are effected in different ways in this compound. To take this as a support for a breakdown to or formation from the molecules P_2MX_2MP and P cannot be correct. However, with sufficiently bulky substituents on phosphorus the hydrogen-halogen intramolecular repulsive interactions should probably force either the monomer $AgXP_2$ or the dimer P_2AgX_2AgP to be formed in the solid state.

In solution the following molecular species are proposed: $Ag_2Cl_2(PMe_3)_4$ (in C_6H_6),⁴⁶ $AgCl(P(p\text{-tolyl})_3)_2$ (in CH_2Cl_2),⁵⁵ $AgX(Ph_2P(C_6H_4CH_2CH=CH_2))_2$, $X=Cl, Br, I$ (in $CHCl_3$),⁵⁶ $AgI(P(C_6H_4-CF_3)Et_2)_2$ (in C_6H_6) and $AgI(PPhMe_2)_2$ (in C_6H_6).^{48,57} That both dimeric and monomeric molecules are proposed to exist in solution supports the above suggested systematization.

$AgXP_2$ -type, bidentate ligands

Four structures of $AgXP_2$ -type, where P_2 is a ditertiary phosphine, have been determined through X-ray diffraction. Three of these, $AgXPSP$, $X=Cl$ and I , and $AgClPC_5P$ are described in this study.¹⁻³ In addition, the structures of $MCl(P..P)$ where $M=Cu, Ag$ and Au and $P..P$ is the ligand 2,11-bis(diphenylphosphinomethyl)benzo(c)phenanthrene have been determined and compared.⁵⁸

The ligand PSP, although potentially tridentate, acts towards silver as bidentate and forms in the solid state, as does PC_5P , dimeric molecules with silver halides (Figs. 2b and 3b). Degischer suggests a monomeric $AgXPSP$ complex in which silver should be tetrahedrally surrounded by one halide ion and the three donor atoms of PSP.¹⁸

For $MCl(P..P)$ the ligand forces a monomeric complex to be formed,⁵⁹ in which silver is three-coordinated. Conductivity measurements in nitromethane and acetonitrile indicate that for the $MCl(P..P)$ series the ionicity of the $M-Cl$ bond increases in the order $Cu < Ag < Au$. This is reflected in the increasing $P-M-P$ angles, 131.9(1), 140.7(1) and 175.7(1)⁰, respectively, for the three metal complexes. It is hereby documented that it is possible to prepare a monomeric three-coordinated silver complex, as was suggested in the previous section. In Table 6 structural parameters of the four silver compounds are given.

Table 6. Distances (Å) in silver halide tertiary phosphines of AgXP₂-type.

Compound	Ag-P	Ag-X	Ag-X (mean value)	X-X	Reference
AgCl(PPh ₃) ₂	2.467(2) 2.472(2)	2.596(2) 2.741(2)	2.67(10)	3.710(2)	4
AgBr(PPh ₃) ₂ CHCl ₃	2.513(7) 2.479(6)	2.742(4)	2.742(4)	4.030(6)	17
AgClIPSP	2.481(4) 2.461(4)	2.686(4) 2.643(4)	2.665(30)	3.786(8)	1
AgIPSP	2.461(2) 2.461(2)	2.911(1) 2.879(1)	2.895(23)	4.323(1)	2
AgClPC ₅ P	2.472(3) 2.492(3) 2.493(4) 2.499(4)	2.664(4) 2.718(3) 2.678(3) 2.663(3)	2.681(26)	3.769(4)	3
AgCl(P..P) ^a	2.458(3) 2.411(3)	2.514(4)	2.514(4)	-	58

a) Ag is three-coordinated. (P..P) means the ligand 2,11-bis(diphenylphosphinomethyl)benzo(c)phenanthrene.

When comparing the dimeric structures of AgXP_2 -type, where P_2 is a ditertiary phosphine or two monotertiary, the following conclusions can be made:

- the Ag-P distances are almost equal, 2.461(4)-2.513(7) Å. The distances are not affected by the nature of X,
- the Ag-Cl distances vary between 2.596(2)-2.741(2) Å. These values are greater than the sum of the tetrahedral covalent radius of silver and the covalent single bond radius of Cl, 2.51 Å,²⁵
- the X-X distances are close to the expected van der Waals distances, 3.60, 3.90 and 4.30 Å for Cl--Cl, Br--Br and I--I, respectively.²⁵

The first two conclusions will be discussed in the sections Variations in the Ag-P bond distances, p. 26, and Variations in the Ag-X bond distances, p. 28, later in this study.

The third conclusion shows that intramolecular X--X repulsive interactions are of importance in determining the geometry of the AgX_2Ag core.

Several reports concerning silver halide complexes with ditertiary phosphines are found in the literature. For reviews, see refs. 36 and 70. In many of these reports suggestions are made of the structures. However, it is not possible to systematize the solid state structures of silver halide ditertiary phosphines until more compounds have been structurally determined.

AgXP_3 -type

The only solid state structure of this type that has been determined up to now is $\text{AgCl}(\text{PPh}_3)_3$.⁵ Compared to copper in $\text{CuCl}(\text{PPh}_3)_3$, the tetrahedral configuration around silver is more distorted (cf. p. 16 and refs. 5 and 27). In the copper compound more severe intramolecular repulsive hydrogen-chlorine interactions probably cause the triphenylphosphine ligands to come closer, giving an almost ideal tetrahedral configuration around the metal atom. If heavier halide atoms were introduced around silver the tetrahedron should probably become more regular. For sufficiently bulky tertiary phosphines and heavy halide atoms the monomeric compounds of AgXP_3 -type should not exist for steric reasons.

In solution monomeric molecules of $\text{AgCl}(\text{PMe}_3)_3$ (in C_6H_6)⁴⁶ and $\text{AgX}(\text{P}(\text{p-tolyl})_3)_3$, X=Cl, Br, I (in CH_2Cl_2) are proposed.⁵⁵

AgXP₄-type

Compounds of this type are AgCl(PMe₃)₄⁴⁶ and AgX(P(p-tolyl)₃)₄, X=F, Cl, Br and I.⁵⁵ No structure determinations have been reported. The silver atoms are thought to be tetrahedrally surrounded by four phosphorus atoms. The halide ions are not coordinated. However, both in solution and in the solid state a phosphine elimination reaction giving AgX(PR₃)₃ and free PR₃ is proposed.^{46,55}

Variations in the Ag-P bond distances

The Ag-P bond distances increase as expected when the number of coordinated phosphorus atoms increases around silver. In Fig. 6 the Ag-P distances for a large number of silver halide phosphines and complexes not containing halide atoms are plotted against the number of coordinated phosphorus atoms. The numbers by the dots refer to Table 7.

In Fig. 6 it can be seen that with one coordinated P atom the Ag-P distances are between 2.35-2.48 Å. For complexes with two coordinated P atoms these distances range between 2.41-2.52 Å. For the only known compound with three P atoms, AgCl(PPh₃)₃, the Ag-P distances range between 2.52-2.56 Å. There is an overlap between the first group distances (one coordinated P) and the second group (two coordinated P). In the following some of these overlaps will be discussed.

In compound 3, polymeric AgSCNP(n-Pr)₃, the Ag-P distance is 2.48(3) Å, in good agreement with the values of Ag-P distances found for the second group. In this structure, however, silver is coordinated rather strongly to N. The Ag-N distance, 2.10(10) Å, is short compared to the normal covalent Ag-N bond distance, 2.22 Å.²⁵ This strong Ag-N bond is formed as the sulphur atom bridges two silver atoms and therefore is a poorer donor than N. The Ag-S distances, 2.83(2) and 2.88(2) Å, are longer than the covalent single bond value 2.56 Å.²⁵

In compound 9, AgSCN(PPh₃)₂, the reverse is found. The Ag-N bond distance, 2.35(2) Å, is longer than 2.22 Å but the Ag-S bond distance, 2.581(6) Å, is in good agreement with the expected single bond value. Here the sulphur atom is bonded to only one Ag atom and evidently the sulphur atom is in this case a better donor than N. The Ag-P distances are 2.455(3) and 2.503(5) Å.

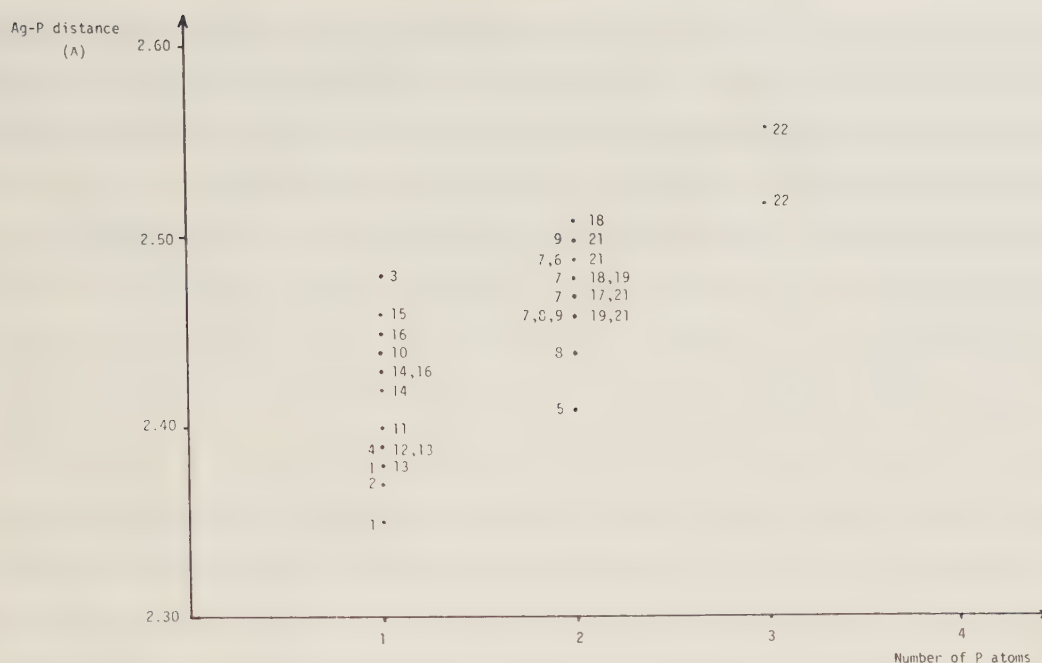


Fig. 6. The variation in Ag-P bond distances with respect to the number of coordinated P atoms. The numbers in the figure refer to Table 7. Silver halide phosphine complexes are placed to the right of the dots and other silver phosphine complexes are placed to the left.

Table 7. Silver phosphine complexes denoted in Fig. 6.

Number	Compound	Ref.	Number	Compound	Ref.
1	$\text{Ag}(\text{O}_2\text{CMe})(\text{PPh}_3)$	60	12	AgClPEt_3	14
2	$\text{AgNO}_3\text{PPh}_3$	61	13	AgClPPh_3	12
3	$\text{AgSCNP}(\text{n-Pr})_3$	62	14	AgBrPPh_3	17
4	$\text{RhAg}_2(\text{C}\equiv\text{C}_6\text{F}_5)_5(\text{PPh}_3)_3$	63	15	$\text{AgIPPh}_3(\text{cubane})$	13
5	$\text{AgNO}_3(\text{P}(\text{OMe})_3)_2$	64	16	$\text{AgIPPh}_3(\text{chair})$	13
6	$\text{PhC}\equiv\text{CAgPMe}_3$	65	17	$\text{AgCl}(\text{PPh}_3)_2$	4
7	$(\text{Ag}(\text{PPh}_3)_2)_3\text{M}(\text{O}_2\text{C}_2\text{S}_2)_3$, M=Fe, Al	66	18	$\text{AgBr}(\text{PPh}_3)_2\text{CHCl}_3$	17
8	$(\text{Ag}(\text{PPh}_2\text{Et})_2)_2\text{Ni}(\text{S}_2\text{C}_2(\text{CN})_2)_2$	67	19	AgClPSP	1
9	$\text{AgSCN}(\text{PPh}_3)_2$	68	20	AgIPSP	2
10	AgIPEt_3	15	21	AgClPC_5P	3
11	AgBrPEt_3	14	22	$\text{AgCl}(\text{PPh}_3)_3$	5

For the halide compounds of the first group the Ag-P distances clearly depend on which halide ion is present. The distances in 12 and 13 belong to chlorine compounds, 11 and 14 to bromine and 10, 15 and 16 to iodine compounds (Table 7). The Ag-P distances in the first group increase in the series $\text{Cl} < \text{Br} < \text{I}$, thus reflecting the increasing donor abilities of the halide ions. In the first group an iodine atom is therefore almost as good a donor as phosphorus giving Ag-P distances equal to those found in compounds in the second group. In compounds of AgXP_2 -type the Ag-P distances do not depend on which halide ion is present.

The reason for these variations in Ag-P distances is probably electronic. The acceptor ability of silver is still great when one P is coordinated but decreases when two P atoms are coordinated. Therefore the coordination of a halide or pseudohalide ion affects the silver-phosphorus relations according to their different donor capacities in the first group but not to the same extent in the second group.

On the contrary, the importance of different substituents on phosphorus is demonstrated in the second group. In compound 5, $\text{AgNO}_3(\text{P}(\text{OMe})_3)_2$, the Ag-P distances, 2.411(3) and 2.412(3) Å, are short compared to those of the other compounds. This shortening can be explained by the greater π -acidity of phosphorus in phosphites compared to phosphines. However, another explanation is based on the oxygen electron withdrawing effects on the electrons in the donor orbitals of phosphorus.⁶⁹ Thus the lone-pair of phosphorus is slightly contracted. To maintain an unaffected bond order the phosphorus atoms in phosphites should come closer to silver, if possible for steric reasons. Consequently, when Ag-P distances, where P belongs to a phosphite ligand, are compared to Ag-P distances, where P belongs to a phosphine ligand, these oxygen effects should be kept in mind.

The number of structurally investigated silver halide phosphines of the AgXP_2 - and especially the AgXP_3 -type are few and more data are needed for a systematization of the variations.

Variations in the Ag-X bond distances

The halide atoms are in silver halide tertiary phosphines of three types: terminal, doubly and triply bridging, cf. p. 18. Examples can be seen for $\text{AgCl}(\text{PPh}_3)_3$ (terminal) in Fig. 5, $\text{AgCl}(\text{PPh}_3)_2$ (doubly) in Fig. 4 and for AgClPPh_3 (triply) in Fig. 1. The distances from a triply or doubly bridging

halide ion to silver vary within some limits. The lower limit is the sum of the tetrahedral covalent radius of Ag and the single bond radius of the halide atom. This lower limit need not be reached for every compound. In Tables 5 and 6 the Ag-X distances are presented. In Fig. 5c selected distances for $\text{AgCl}(\text{PPh}_3)_3$ are given. To exemplify that Ag-X distances between silver and terminal, doubly and triply bridging halide ions can have almost the same values, see the Ag-Cl distance in $\text{AgCl}(\text{PPh}_3)_3$, 2.552(1) Å, the minimum distance in $\text{AgCl}(\text{PPh}_3)_2$, 2.596(2) Å, and in AgClPPh_3 , 2.532(3) Å. These values are close to or slightly longer than the expected value, 2.51 Å.²⁵

Within the compounds AgClPSP , AgClPC_5P , $\text{AgBr}(\text{PPh}_3)_2\text{CHCl}_3$, AgIPet_3 and AgIPSP the Ag-X distances are almost equal (Tables 5 and 6). The mean Ag-I(triply) bond distance in AgIPet_3 and the mean Ag-I(doubly) bond distance in AgIPSP agree well, i.e. 2.919(1) and 2.895(23) Å. The Ag-Cl(doubly) bond distances in AgClPSP and AgClPC_5P are as expected almost equal, i.e. 2.665(30) and 2.681(26) Å. The latter values are approximately 0.12 Å longer than the Ag-Cl(terminal) bond distance in $\text{AgCl}(\text{PPh}_3)_3$, i.e. 2.552(1) Å. Although more structural data are needed it seems that for these compounds the Ag-X distances for a given X follow the sequence:

$$\text{Ag-X(terminal)} < \text{Ag-X(doubly bridging)} \approx \text{Ag-X(triply bridging)}.$$

For the other compounds containing doubly and triply bridging halide atoms the Ag-X distances are more or less distributed around these mean values (Tables 5 and 6).

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